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(54) Title: SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF CONTAMINANTS FROM ION EXCHANGE RESINS (57) Abstract A method for extracting leachable contaminants from ion exchange resins comprises exposing the resin to supercritical carbon dioxide for a sufficient interval of time to allow at least a portion of the leachable contaminant to be solubilized by the supercritical carbon dioxide; followed by removal from the resin of the supercritical carbon dioxide having the leachable contaminant dissolved therein. The method is particularly useful for removing organic contaminants, which may or may not contain sodium or chlorine, from the resin, to thereby provide ion exchange resins which are suitable for critical use applications in the nuclear, electronics, pharmaceutical and food industries.		

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SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF CONTAMINANTS FROM ION EXCHANGE RESINS

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FIELD OF THE INVENTION

The present invention relates to a method of removing contaminants from ion exchange resins, and more specifically to the use of supercritical carbon dioxide for the removal of leachable
10 organic and inorganic materials from commercial ion exchange resins to thereby produce ion exchange resins acceptable for use in critical applications.

BACKGROUND OF THE INVENTION

Ion exchange resins are widely used in the production of highly pure water in the nuclear,
15 electronics (semi-conductor), pharmaceutical and food industries. In the nuclear industry, for example, ion exchange resins are used for purification of nuclear process water.

The problem exists that commercial grade ion exchange resins contain varying quantities of organic and inorganic impurities which have a tendency to leach out of the resin during use. Many
20 of these impurities arise during manufacture of the resin, and include monomers and oligomers of the polymer from which the resin beads are formed, as well as impurities in the starting materials. These impurities may become functionalized, for example, with sulphate or amino groups during functionalization of the resin.

25 Due to the presence of leachable impurities, commercial ion exchange resins must be treated prior to use in critical applications where extraneous organic materials are unacceptable. Presently used purification methods include a variety of proprietary techniques, most of which are based on extraction of leachable impurities by organic solvents. In one of these methods, the resin is washed with a series of solvents of decreasing polarity. In addition to being slow, costly and wasteful, this
30 process suffers from a number of other disadvantages. Firstly, it is not very effective. Organic solvent molecules are relatively bulky and cannot effectively penetrate into the interior of the cross-linked resin beads to leach out the impurities contained therein. Secondly, solvent treatments may require high temperatures and pressures, which may damage the integrity of the resin beads, for example by de-crosslinking, or facilitating loss of functional groups. Thirdly, the organic solvents
35 used to wash the resin may be absorbed by the resin beads, resulting in further contamination.

Therefore, there is a need for a more economical and effective method for removing leachable impurities from commercial ion exchange resins.

SUMMARY OF THE INVENTION

5 The present invention overcomes the above difficulties by providing a method for removing unwanted contaminants from ion exchange resins in which resins are exposed to supercritical carbon dioxide for a period of time sufficient to permit leachable impurities to diffuse out of the resin. The inventors have found that supercritical carbon dioxide is capable of reducing the levels of impurities in commercial ion exchange resins to levels low enough to permit the use of the treated resins in
10 critical applications in the nuclear, semi-conductor, pharmaceutical and food industries.

 The high density, high solvent power and low viscosity of supercritical carbon dioxide allow it to quickly diffuse throughout the entire resin bead, and solubilize the leachable impurities contained in the resin structure. The degree to which leachable impurities are removed by the method of the
15 present invention suggests that supercritical carbon dioxide removes impurities trapped deep inside the cross-linked matrix of the resin beads. This is surprising in that many of the impurities contained within the resin beads are relatively bulky organic molecules which became trapped in the cross-linked matrix during its formation. One would expect that such impurities could only be removed slowly, if at all.

20

 The inventors believe that, during treatment with supercritical carbon dioxide, the cross-linked cage structure of the bead is expanded temporarily under pressure. This expansion is believed to result in escape of organic materials from the interior of the resin bead which ordinarily would leach out very gradually over time.

25

 Furthermore, the inventors have surprisingly found that treatment of ion exchange resins by the method of the present invention results in a resin which has a noticeably higher initial effectiveness than untreated or conventionally treated commercial resins. The inventors believe that this is due to removal of organic impurities on the surface of the bead, which have the effect of
30 reducing the initial activity of the resin.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described, by way of example only, with reference to the following drawings, in which:

Figure 1 is a schematic view of the supercritical carbon dioxide extraction apparatus used in
5 the Examples;

Figure 2 is a graphical representation of the FID profile of leachate from Ambersep 440E ion exchange resin before and after supercritical carbon dioxide extraction;

10 Figure 3 is a graphical representation of the FID profile of leachate from Amberlite 120 Plus/H ion exchange resin before and after supercritical carbon dioxide extraction;

Figure 4 is a graphical representation of the effect of supercritical carbon dioxide extraction on C-14 uptake by Ambersep 440E/OH ion exchange resin before regeneration to the OH form;

15 Figure 5 is a graphical representation of the effect of supercritical carbon dioxide extraction on C-14 uptake by Ambersep 440E/OH ion exchange resin after regeneration to the OH form;

20 Figure 6 is a graphical representation of the effect of supercritical carbon dioxide extraction on the C-14 capacity of Ambersep 440E/OH ion exchange resin after regeneration to the OH form; and

Figure 7 is a graphical representation of the effect of supercritical carbon dioxide extraction on Co-60 uptake by Amberlite IR 120 Plus ion exchange resin.

25 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The method of the present invention may preferably be used to reduce the amounts of at least three types of impurities in ion exchange resins, namely functionalized or unfunctionalized
30 hydrocarbon molecules, chlorine-containing impurities and sodium-containing impurities. These three categories may overlap to some degree since a portion of the hydrocarbon impurities may contain chlorine and/or sodium.

Ion exchange resin beads are generally comprised of a cross-linked polymer matrix formed by polymerization of styrene combined with as a cross-linking agent such as divinylbenzene. The polymerized product invariably contains amounts of unreacted monomers and oligomers, and these are the main sources of hydrocarbon impurities. Other sources of impurities include those contained
5 in the monomeric starting materials used to form the resin beads, as well as other reagents added during the polymerization, for example to control reactivity. During functionalization of the resin, some of these impurities may also undergo functionalization, for example by sulfonation (cation resin) or, to a lesser extent, by aminomethylation (anion resin).

10 Previous studies (for example Wataru Agui, Masahito Takeuchi, Masahiko Abe, and Keizo Ogino, "*A Removal of Leachables from Strong Acid Cation Exchange Resins*", Journal of Japan Oil Chemists' Society (Yukagaku), Vol. 38, No. 5, p 405-414, 1989) have identified several organic impurities in strong acid cation exchange resins ranging in molecular weights from about 500 to about 5,000, and have also revealed the presence of lower molecular weight compounds such as
15 monomeric aromatic sulphonates such as p-sulphobenzoic acid and p-hydroxybenzenesulphonic acid.

The quantities of organic impurities present in an ion exchange resin is usually expressed as the level of total organic carbon (TOC). Commercially available "standard grade" resins generally contain relatively high TOC levels, often exceeding 10 mgC/dm³ (Clarence D. Colley, Prepared
20 Discussion of IWC -90-19, "*A Comparison of Operational Data from Three Type I Gel Anion Resins*", Proceedings of the International Water Conference, Pittsburgh, Penn., Oct 21-24, 1990). High TOC levels in a resin can cause unwanted colour in the process water, and generally render such resins unsuitable for critical applications.

25 Government regulations pertaining to the use of ion exchangers and adsorbents for the processing of water, food, beverages, pharmaceutical and medical products are discussed in a recent overview (R. Kunin, "*Introductory Overview*", Reactive Polymers, Vol. 24, No. 2, pp. 79-89, 1995).

In the preparation of anion exchange resins, chloromethylation is an essential intermediate
30 step prior to functionalization with amines, and is the likely source of various chlorine containing organic compounds which are typically found in the resin matrix. Chloromethylation is not used in the preparation of cation resins and therefore, anion resins typically contain higher levels of chlorine than cation resins. Low chloride anion resins suitable for critical applications are available from

several suppliers. Analysis of these resins show levels of chlorine ranging from 57 to 1675 $\mu\text{g/kg}$ (B.R. Nott, "An Evaluation of Nuclear Grade Ion Exchange Resins", Ontario Hydro Research Division Report No. 81-42-H, March 4, 1981), likely including both organic and inorganic chlorine compounds.

5

The chlorine content of ion exchange resins used in nuclear applications must be relatively low, and preferably no higher than 70 mg Cl/kg of moist resin, due to the possibility of chloride-induced stress corrosion cracking of stainless steel components in nuclear reactors.

10 Sodium may be present in ion exchange resins as a salt of residual organic acids such as organic sulfonic acids and residual regenerants. In order to minimize neutron activation products in nuclear reactors, the maximum acceptable level of sodium in new resins for CANDU reactors has been specified as 100 mgNa/kg of moist resin (Ontario Hydro Standard Specification No. M-678-86, January 1986, and Draft No. 1 of *Revision to Standard Specification for Resin, Ion Exchange*,
15 *Nuclear Grade Type: Strong Acid/Strong Base*, Material Management Department Document No. M-678-xx (not issued yet) , File 178.2-929-7, Job S0193, Dec 15, 1988).

Extraction of leachable impurities from ion exchange resins using supercritical fluids offers several key advantages over known methods using liquid solvent washes. For example, the low
20 viscosity and high solute diffusivity of supercritical fluids provide superior mass transfer characteristics and thereby enable faster extraction fluxes, and the low surface tension of supercritical fluids enables superior penetration into microporous solid matrices.

The preferred supercritical fluid used to extract impurities in the method of the present
25 invention is supercritical carbon dioxide, which is non-toxic, inexpensive, recyclable, and possesses a low critical temperature (31 °C) and pressure (1071 psi). The inventors have found that extraction under these supercritical conditions surprisingly does not adversely affect the chemical reactivity of ion exchange resins and, as discussed in more detail below, actually increases the initial activity of ion exchange resins.

30

The method of the present invention is preferably carried out in a conventional supercritical extraction apparatus, comprising a source of supercritical carbon dioxide, typically a storage and supply cylinder, an extractor vessel and a scrubber. A quantity of resin beads is loaded into the

extractor vessel, which is then sealed. Carbon dioxide is then supplied from the source to the vessel through a pressure line under supercritical conditions, that is, at a temperature of at least 31°C and a pressure of at least 1,071 psig. The resin is exposed to the supercritical carbon dioxide in the vessel for a period of time depending on the amount of leachable material to be extracted from the resin.

5 At the end of this time, the supercritical carbon dioxide containing extracted impurities is drained from the vessel and is allowed to expand to its gaseous state as it passes through the scrubber, thereby separating out the organic and inorganic contaminants, which are generally either liquids or solids. The scrubbed carbon dioxide is then vented through an exhaust to the atmosphere or may alternatively be recycled and recompressed and returned to the supercritical carbon dioxide storage

10 and supply cylinder.

In particularly preferred embodiments of the invention, the interior of the extractor vessel is maintained at a temperature of at least about 31°C which does not result in damage to the resin beads. Preferably, the temperature is not higher than about 100°C, and is more preferably from

15 about 40 to about 70°C, even more preferably from about 50 to about 60°C, and most preferably about 55°C.

During the extraction, the pressure inside the extractor vessel is preferably maintained at not less than about 1,071 psig, in order to maintain the carbon dioxide in a supercritical state, and

20 preferably is not raised to a pressure at which the resin beads are damaged. The inventors have found a suitable upper limit for the pressure to be about 5,000 psig. Preferably, the time of extraction is at least about ½ hour, more preferably from about ½ to about 3 hours, and even more preferably from about ½ to about 1 hour, depending on the extraction conditions and the amount of impurities which are to be removed.

25

In general, the higher the mechanical compression of a supercritical fluid, the higher its solvent power. The inventors have found the variation in solvent power brought about by varying the pressure actually increases the efficiency of the extraction, most likely due to the fact that the variation in solvent power causes the supercritical carbon dioxide to leach out impurities of various

30 polarities, similar to using a series of liquid solvents of varying polarities to wash out a range of impurities. Most preferably, the pressure inside the extractor vessel is gradually increased from about 1,071 psig during the course of the extraction in order to achieve the desired progression in solvent power. More preferably, the pressure in the extractor vessel is gradually raised during the extraction

from about 1,071 psig to about 5,000 psig over a period of about 30 minutes and is held at 5,000 psig for the remainder of the extraction, which may preferably comprise an additional 30 minutes.

Another particularly preferred embodiment of the present invention involves using "dynamic" conditions during the extraction, meaning that a flow of supercritical carbon dioxide into and out of the extractor vessel is maintained during at least part of the extraction process. Preferably, the flow rate of supercritical carbon dioxide into the vessel is the same as the flow rate leaving the vessel, such that the pressure and temperature conditions inside the vessel remain constant. In a particularly preferred embodiment, the extraction is carried out over a period of about 15 minutes under static conditions, after the temperature and pressure have reached a steady state, followed by 15 minutes under dynamic conditions with a flow rate of supercritical carbon dioxide of 20 mL/min. through the vessel.

The inventors have also found that the method of the invention is also effective to increase the initial operating capacity of ion exchange resins, particularly anion exchange resins, most likely due to the removal of organic impurities which block reactive sites on the surface of the resin bead. The method of the invention is also expected to increase the useful life of ion exchange resins, particularly anion resins, by reducing the incidence of fouling caused by coating of the surface of the anion resins with organic sulfonic acid impurities leached from the resin beads over time.

20

In addition, the method of the invention is expected to permit regeneration of ion exchange resins which have been fouled by organic impurities other than those which are leached from the resin matrix of the ion exchange resin. Specifically, the method of the invention is expected to be useful in "cleaning up" anion exchange resins which have become fouled by water-borne organics found in natural water, for example humic acid, fulvic acid, tannins, lignins and other products from plant decay.

25

An additional advantage of the method of the invention is that the treatment of an anion resin with supercritical carbon dioxide is expected to convert the resin from its chloride form to either its carbonate or bicarbonate form. Anion resins must typically be converted from their chloride form to their hydroxide form prior to use. However, the chloride form cannot be quantitatively converted to the hydroxide due to selectivity coefficients of the resin. Therefore, in the prior art an intermediate step has typically been used to first convert the resin from the chloride form to the carbonate,

30

bicarbonate or bisulfate form, followed by treatment with sodium hydroxide to convert the resin to its hydroxide form. This intermediate step is effectively eliminated by the method of the present invention.

5 EXAMPLES

The effectiveness of the method of the invention in removing contaminants from ion exchange resins is now illustrated by a series of examples in which a number of different ion exchange resins are examined for leachable contaminants both before and after supercritical carbon dioxide extraction.

10

In the following examples, all supercritical carbon dioxide extractions were carried out under static conditions at 55°C and 5000 psig using a Supercritical Extraction Screening System (Catalogue No. 08U-06-60-FS) from Autoclave Engineers Group, Erie, PA, with a maximum operating pressure of 6000 psi at 460°F, and a tubular extractor vessel of 75 mL volume. High purity supercritical
15 carbon dioxide from Union Carbide was used throughout. The experimental set-up used is schematically illustrated in Figure 1. The conditions chosen for supercritical CO₂ extractions did not appear to affect the physical integrity of the resin. The effect of supercritical CO₂ on resin samples was studied using several characteristics.

20 Example 1 - Total Organic Carbon (TOC) in Water Extracts

Water extractable organics from resin samples were determined by continuously shaking 20 g of the resin before supercritical carbon dioxide extraction or 5g of resin after supercritical carbon dioxide extraction in 50 mL of deionized water at 55°C for 72h.

25 Table 1 shows the results of water extractions of several commercially available resins before and after extraction with supercritical carbon dioxide. Ambersep™ 440E/OH is the strong base anion resin that is used by Rohm and Haas Company to produce low chloride nuclear grade IRN™ 78 by a proprietary process, and Amberlite™ IR 120 Plus/H is the corresponding precursor for the nuclear grade strong acid cation resin, IRN 77. It is interesting to note from Table 1 that both
30 nuclear grade resins IRN 77 and IRN 78 appear to have higher levels of leachable organics in their matrices. It is not clear whether this is a result of their proprietary treatment. The anion generally makes a greater contribution to the TOC value due to the more unstable amine functional group (F.P. Scanlan and J.F. Muller, "An Analytical Investigation of the Thermal Degradation of a Cation-

Exchange Resin - Part 2", Journal of Analytical and Applied Pyrolysis, Vol. 16, pp. 269-289, 1989; Shing-Jen Shiao and Chiao-Ming Tsai, "*Stability of Anion Resin*", Nuclear Science Journal, Vol. 27, No. 6, p 523-536, 1990). The high TOC value shown in Table 1 for IRN 78 after the supercritical CO₂ extraction is suspect and it is more than likely due to an analytical error.

Table 1

Water-Extractable Organics in Ion Exchange Resins as Total Organic Carbon (TOC)-(in µg/g of resin)

Sample	Description	TOC before SC-CO ₂	TOC after SC-CO ₂	% Removal
Ambersep 440E/OH	Strong Base Anion Resin (SBA)	127	106	16
Amberlite IR 120 Plus/H	Strong Acid Cation Resin (SAC)	157	127	19
IRN 77	Strong Acid Cation Resin (SAC)	233	198	15
IRN 78	Strong Base Anion Resin (SBA)	208	413	-98
IRN 150	Mixed-Bed of SAC +SBA	14	22	-57
IRN 154	*Mixed-Bed of SAC + SBA	25	-	-
"Blank" (deionized water with no resin added)	-	0.9	-	-

*Strong Acid Cation Resin in Lithium form

Thus, it can be seen that a 15-19% change in the water-extractable organics is brought about by supercritical carbon dioxide extraction. These samples were analyzed following filtration through 0.2µm filters, and hence these measurements reflect only soluble organic residues, and not the total reduction of the organic residues from the resin. The anion resin samples appeared lighter and brighter after the supercritical CO₂ extraction, and more importantly produced a significantly

diminished odour. Supercritical CO₂ is a non-polar solvent and hence highly polar and insoluble materials may not have been extracted completely. This problem can be addressed through use of co-solvents such as methanol which enhances the solubilizing power of the extracting medium (R.F. Cross, J.L. Ezzell, N.L. Porter, and B. E. Richter, "*Fluid Composition Sources and Flexibility in Supercritical Fluid Extraction*", American Laboratory, 12-17, August, 1994).

Example 2 - Elemental Analysis for Chemical Composition

In order to gain an insight into the nature of any chemical compositional changes in the resin brought about by the extraction with supercritical CO₂, the samples of ion exchange resins were analyzed for their elemental composition before and after the supercritical CO₂ extraction. The elemental analysis including total chlorine and sodium analysis of resin samples were performed by Chemisar Laboratories Inc., Guelph, Ontario. The results are summarized in Tables 2 and 3.

Table 2
Elemental Analysis of IX Resins (%)

Sample	Description	*Before SC-CO ₂						After SC-CO ₂					
		C	H	N	O	S		C	H	N	O	S	
Ambersep 440E/OH	Strong Base Anion Resin (SBA)	37.51	10.53	2.62	48.34	-		37.89	9.82	2.72	44	-	
Amberlite IR 120 Plus/H	Strong Acid Cation Resin (SAC)	33.45	7.26	-	48.86	10.89		28.81	7.29	-	49.88	9.44	
IRN 77	Strong Acid Cation Resin (SAC)	28.69	7.78	-	48.43	9.4		29.15	7.58	-	50.43	9.49	
IRN 78	Strong Base Anion Resin (SBA)	34.81	10.69	2.81	45.03	-		37.97	6.28	2.86	45.83	-	
IRN 150	Mixed-Bed of SAC +SBA	45.71	9.96	3.28	38.15	0.3		37.99	8.26	1.42	38.26	5.95	
Potassium Hydrogen Phthalate (submitted as an “unknown”)	Monopotassium salt of aromatic dicarboxylic acid	46.62 (47.05)	2.39 (2.47)	0.03 (0.00)	31.03 (31.34)	-		-	-	-	-	-	

* The expected percentages are shown in parentheses.

The percentage of elements in the composition is a function of the moisture content of the resin and this is likely to change as a result of the supercritical CO₂ extraction. The ratio of C: N and C:S is generally a good indication of the relative amounts of functional groups present in the resin. The results shown in the Tables clearly indicate that no significant change in the functional groups has been brought about by the extraction with supercritical carbon dioxide.

Table 3

Impact of SC-CO₂ Extraction on Functional Group Distribution

	Sample	Description	Ratio of Elements before SC-CO ₂			Ratio of Elements after SC-CO ₂		
			C/N	C/S	H/O	C/N	C/S	H/O
10	Ambersep 440E/OH	Strong Base Anion Resin (SBA)	16.69	-	3.46	16.24	-	3.54
15	Amberlite IR 120 Plus/H	Strong Acid Cation Resin (SAC)	-	8.21	2.36	-	8.15	2.32
	IRN 77	Strong Acid Cation Resin (SAC)	-	8.15	2.55	-	8.19	2.39
20	IRN 78	Strong Base Anion Resin (SBA)	14.44	-	3.77	15.47	-	2.17
	IRN 150	Mixed-Bed of SAC +SBA	51.27	1284	4.14	31.18	17.04	3.43

25 *The average chlorine content from NAA of 5 X 1g samples of IRN 78 had been found to be 60 µg/g resin (B.R. Nott, "Electrolytic Process for Producing Extremely Low Chloride Anion Exchange Resins", US Patent No. 4690739, Sept. 1/1987). After processing, this value was reduced to 30 µg/g resin.

30 The significant change in the C:S ratio for IRN 150 after the SC-CO₂ extraction may be due to the inhomogeneity of the mixed-bed sample taken for analysis.

In order to avoid the effects of variable amounts of water and the possible conversion

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of the resin to its carbonate form during supercritical CO₂ extraction, the elemental analysis was performed on pre-treated and vacuum dried resin samples. The pre-treatment consisted of converting a batch of Ambersep 440E resin into carbonate form, wet-sieving to fractions held between US mesh 30 and 40, and removing free water under standard conditions to produce moist resin. After
5 supercritical CO₂ extraction, the resin was dried in a vacuum desiccator to constant weight. The strong acid cation resin was not regenerated but otherwise was treated the same way. The results of this analysis are shown below in Table 4.

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Table 4
Elemental Analysis of Vacuum-dried IX Resins (%)
 (Anion resin in the carbonate form; average of two analyses)

Sample	Description	Before SC-CO ₂					After SC-CO ₂				
		C	H	N	O	S	C	H	N	O	S
Ambersep 440E/OH	Strong Base Anion Resin (SBA)	59.47	8.44	4.40	24.26	-	56.77	8.93	4.22	25.33	-
Amberlite IR 120 Plus/H	Strong Acid Cation Resin (SAC)	40.90	5.70	0.03	36.05	13.45	40.56	5.82	0.03	35.16	13.13

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The elemental composition of both anion and cation resin remains essentially unchanged during supercritical carbon dioxide extractions, confirming that no loss of functional groups or the resin integrity.

5 Example 3 -Total Chlorine Content in Resin

As shown below in Table 5, the neutron activation analysis of resin samples for chlorine content before and after supercritical CO₂ extraction shows changes for the anion resin, Ambersep 440E/OH. As mentioned above, previous analysis of low chloride anion resins from several commercial suppliers had produced values ranging from 57 to 1675 µg /kg. The corresponding values for cation resins were 13 to 40µg/kg. The observed 20% change in the chlorine content for the anion resin in Table 5 is attributable to extraction of organochlorines from the resin matrix.

Table 5
Neutron Activation Analysis of Chlorine in Resins (ppm)

Sample	Description	Before SC-CO ₂	After SC-CO ₂	% Removal
Ambersep 440E/OH	Precursor of Nuclear grade Strong Base Anion Resin (SBA)	120	94	21.7
Amberlite IR 120 Plus/H	Precursor of Nuclear Grade Strong Acid Cation Resin (SAC)	<10	<10	0
IRN 77	Nuclear Grade Strong Acid Cation Resin (SAC)	<10	<10	0

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IRN 78	Nuclear Grade Strong Base Anion Resin (SBA)	74	74	0
IRN 150	Nuclear Grade Mixed-Bed of SAC +SBA	45	46	-2.2

5

Example 4 - Total Sodium Content in Resin

The resin samples were analyzed before and after supercritical extraction and the results are given below in Table 6.

10

Table 6**Analysis of Sodium in Resins (%)**

	Sample	Description	Before SC-CO₂	After SC-CO₂	% Removal
15	Ambersep 440E/OH	Precursor of Nuclear grade Strong Base Anion Resin (SBA)	0.037	0.008	78
20	Amberlite IR 120 Plus/H	Precursor of Nuclear Grade Strong Acid Cation Resin (SAC)	0.040	0.032	20
	IRN 77	Nuclear Grade Strong Acid Cation Resin (SAC)	<0.001	<0.001	0
	IRN 78	Nuclear Grade Strong Base Anion Resin (SBA)	<0.001	0.010	N/A

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IRN 150	Nuclear Grade Mixed-Bed of SAC +SBA	0.012	0.002	83
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5 It is seen from Table 6 that anion resin shows a considerable loss of sodium as a result of the supercritical CO₂ extraction. Considering the manufacturing steps involved, anion resin is much more likely to possess sodium impurities from reagents. The fact that most of them are removed by supercritical CO₂ treatment suggests that they are present in the resin as somewhat less polar sodium salts of organic acids. The cation resin, as would be expected, experiences
10 relatively lower sodium removal.

Example 5 - FID Profile of Leachates by SFE/SFC

Attempts to obtain FT-IR spectra of extractables from supercritical fluid extraction (SFE) coupled with supercritical fluid chromatography (SFC) were not successful due to relatively large
15 amounts of water associated with the resin. Even use of several drying agents such as Celite (3:1) and Hydromatrix (3:1) was not helpful. Hence the extracts were characterized by a flame ionization detector.

FID profiles of leachates were obtained by the Department of Chemistry of Virginia
20 Polytechnic Institute and State University, Blacksburg, Virginia, following Supercritical Fluid Extraction (SFE)/ Supercritical Fluid Chromatography (SFC). For SFE, 100mg of sample pre-mixed with 300 mg of Hydromatrix™ (inorganic-based desiccant from Varian Associates) were treated with supercritical carbon dioxide at 60°C and 300 atm., for 15 min at 2 mL/min liquid CO₂ and the extractables trapped in a cryo trap at -10°C. SFC was performed on a cyanopropyl
25 column (10 cm x 1.0 mm) with 5µm (i.d.) particles. The trap temperature was set at 80°C and the elution was performed with supercritical CO₂ at 60°C and 150 atm for 2 min, followed by 15 min linear ramp from 150 -350 atm at the same temperature. The entire on-line analysis was performed on a Suprex MPS/225 instrument and a 3mL vessel and a FID detector.

30 The SFE/SFC process was performed under identical conditions on the commercial grade samples of cation and anion resins before and after supercritical carbon dioxide extraction.

The resultant spectra for Ambersep 440E and Amberlite 120 Plus/H are respectively illustrated in Figures 2 and 3. As can be seen from Figures 2 and 3, the FID profiles of both cation resin and anion resin show fewer and smaller peaks after the supercritical CO₂ extraction. These peaks are due to organic materials that have leached out during SFE/SFC and clearly indicate the reduction of extractables due to exposure to supercritical CO₂.

Example 6 - Effect of Supercritical CO₂ Extraction on Reaction Kinetics

A major step determining the rate of ion exchange reaction is the diffusion of reactants and products to and from the site of exchange (R.R. Harries and M. Ball, "*An Equilibrium Versus Kinetics in Water Purification*". In: P.A. Williams and M.J. Hudson, eds. "Recent Developments in Ion Exchange", Ed, Elsevier Applied Science, (ISBN 1-85166-101-8), 1987: 402-418). Removal of organic residues blocking the passages leading to these exchange sites is expected to enhance the reaction kinetics.

Experiments were conducted to confirm this both with cation exchange and anion exchange reactions with the respective ion exchange resins. These experiments comprised a kinetics study of carbonate exchange which was carried out by exposing the resin (pre-screened to 30 to 40 U.S. mesh size in the carbonate form and reconverted to hydroxide form) to a solution of sodium carbonate traced with ¹⁴CO₃²⁻ and monitoring the C-14 activity change in the supernatant solution by periodic sampling. Similarly, the cobalt uptake was carried out using cobalt nitrate solution containing a trace of Co-60. Both C-14 and Co-60 levels were measured by liquid scintillation counting following calibration with standards.

Figure 4 illustrates the difference in the rate of carbonate anion exchange between the "as-received" form of the Ambersep 440E/OH resin, which is the precursor of the nuclear grade strong base anion exchange resin IRN 78, and the supercritical CO₂ extracted sample of the same resin. There is clearly a significant enhancement in the rate of uptake of the carbonate ion by the resin after the supercritical CO₂ extraction/treatment. However, it should be noted that after the supercritical CO₂ extraction, the counter ion in the resin may have been changed to CO₃²⁻ from the original OH⁻ form. Hence, the experiment was repeated several times after regenerating the resin following supercritical CO₂ extraction, to the OH⁻ form. Still, a noticeable enhancement can

be seen (Figure 5) in the carbonate uptake following supercritical carbon dioxide extraction. The exchange profile from two repeat experiments (samples B and C) are virtually superimposable. It was also observed that in all exchange experiments performed using identical amounts of carbonate solution and resin, the C-14 absorption by the resin reached a maximum at about 60 minutes from the beginning of exposure. The "Blank" solution (with no resin added) run in parallel did not show any significant variation in C-14 content in the solution. This appears to be due to an increase in the pH of the solution brought about by exchanging OH⁻ ions from the resin, followed by absorption of carbon dioxide from the surrounding atmosphere. The carbonate absorption profile shown in Figure 6 is typical of this behaviour. The observations extended later up to 74h indicated further gradual decrease of the C-14 uptake by the resin. At the 60 min absorption maximum, the supercritical carbon dioxide extracted resin showed a 8-10% increase in the uptake of C-14 per g of dry resin. Under dynamic conditions (column runs) this difference is expected to be even larger and could translate to much higher operating capacities.

15 A similar enhancement of the exchange of cations was seen with Amberlite IR 120, which is the precursor for the nuclear grade strong acid cation resin IRN 77 manufactured by Rohm and Haas Co., when cobalt cation uptake was monitored using Co-60 radio tracer. These results are shown in Figure 7.

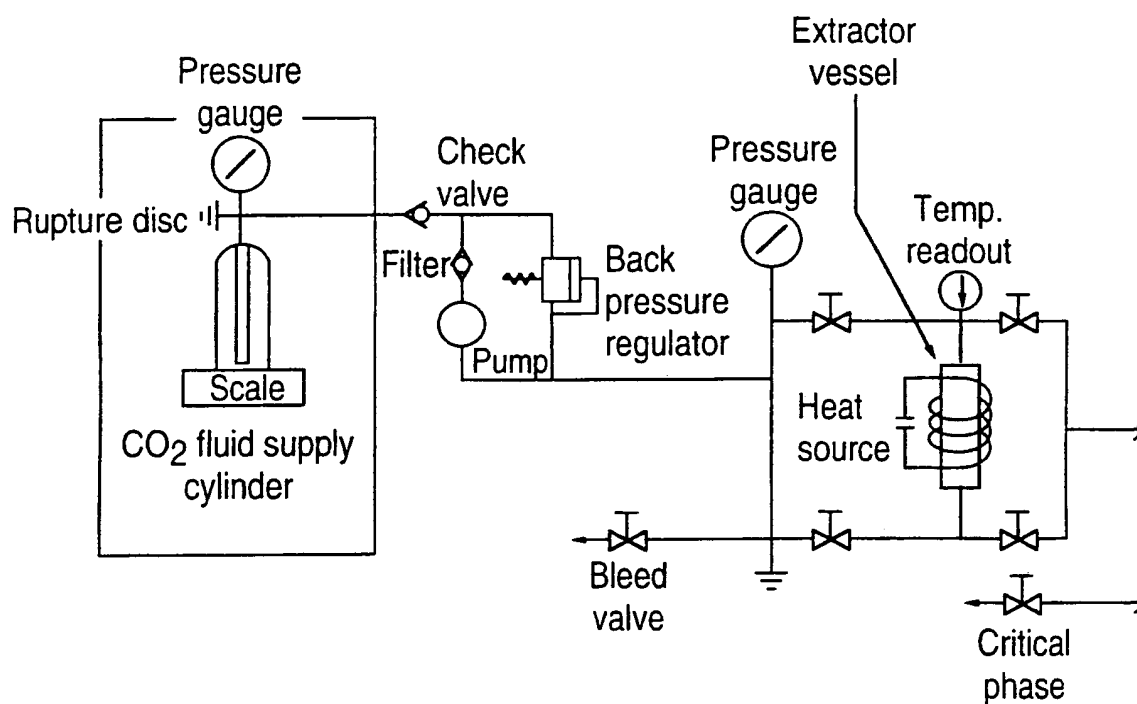
20 Although the invention has been described in connection with certain preferred embodiments, it is to be understood that it is not restricted thereto. Rather, the invention is intended to include all embodiments as may fall with the scope of the following claims.

What is claimed is:

1. A method for extracting a leachable contaminant from an ion exchange resin,
5 comprising:
 - (a) exposing the resin to supercritical carbon dioxide for a sufficient interval of time to allow at least a portion of said leachable contaminant to be solubilized by said supercritical carbon dioxide; and
 - 10 (b) removing from the resin the supercritical carbon dioxide having said leachable contaminant dissolved therein.
2. The method of claim 1, wherein the leachable contaminant is an organic compound.
- 15 3. The method of claim 1, wherein the organic compound contains one or both of sodium and chlorine.
4. The method of claim 2, wherein the organic compound is functionalized with a
20 sulfonic acid group or an amino group.
5. The method of claim 3, wherein the organic compound is functionalized with a sulfonic acid group or an amino group.
- 25 6. The method of claim 1, wherein said step (a) of exposing the resin to supercritical carbon dioxide is carried out at a temperature of at least 31°C and a pressure of at least 1,071 psi.
7. The method of claim 6, wherein said temperature is from 31°C to about 100°C.
- 30 8. The method of claim 7, wherein the temperature is about 55°C.

9. The method of claim 4, wherein the pressure is between 1,071 psi and about 5,000 psi.
10. The method of claim 6, wherein the pressure is about 5,000 psi.
- 5 11. The method of claim 6, wherein said step (a) of exposing the resin to supercritical carbon dioxide is carried out for a period of from about 30 minutes to about 3 hours.
12. The method of claim 11, wherein the resin is exposed to carbon dioxide for a period
10 of about 30 minutes to about 1 hour.
13. The method of claim 6, wherein the pressure is gradually increased from about 1,071 psi to about 5,000 psi at the beginning of said step (a), and the pressure is maintained at about 5,000 psi for the remainder of said step (a).
- 15 14. The method of claim 13, wherein the pressure is gradually increased from about 1,071 psi to about 5,000 psi over a period of from about 30 minutes.
15. The method of claim 1, wherein said method is conducted in an extraction vessel, and
20 wherein at least a portion of said step (a) is conducted under dynamic conditions in which a flow of said supercritical carbon dioxide is maintained into and out said extraction vessel.
16. The method of claim 15, wherein said flow of supercritical carbon dioxide is about 20
25 mL/min.
17. The method of claim 15, wherein said step (a) comprises exposing said resin to supercritical carbon dioxide for about 15 minutes under static conditions and about 15 minutes under dynamic conditions.
- 30

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SCHEMATIC DIAGRAM OF SUPERCRITICAL CARBON
DIOXIDE EXTRACTION SET-UP

FIG.1A

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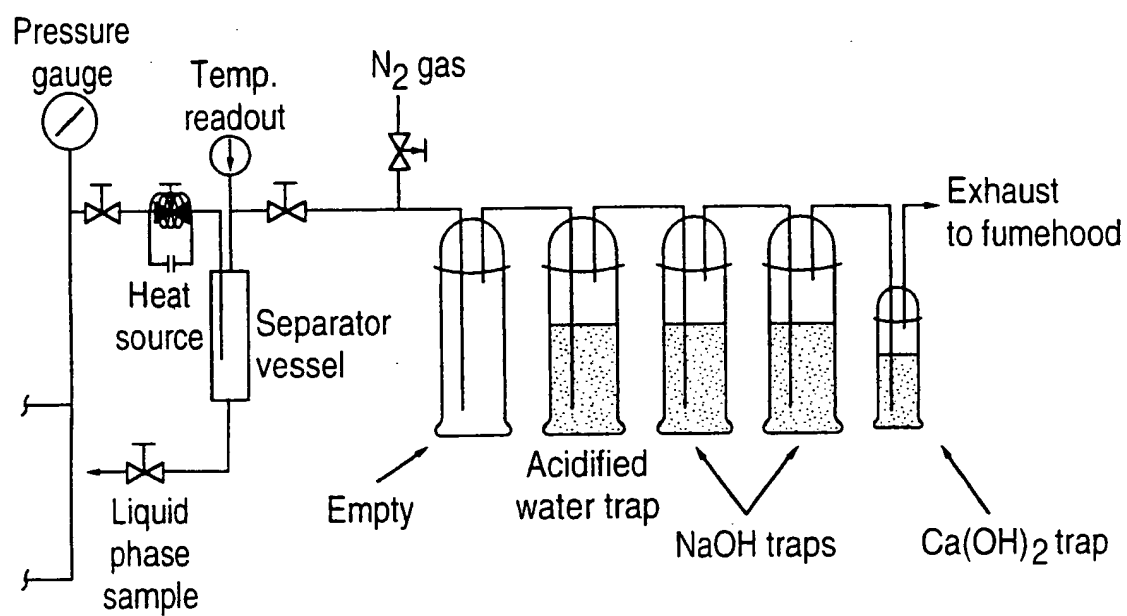


FIG.1B

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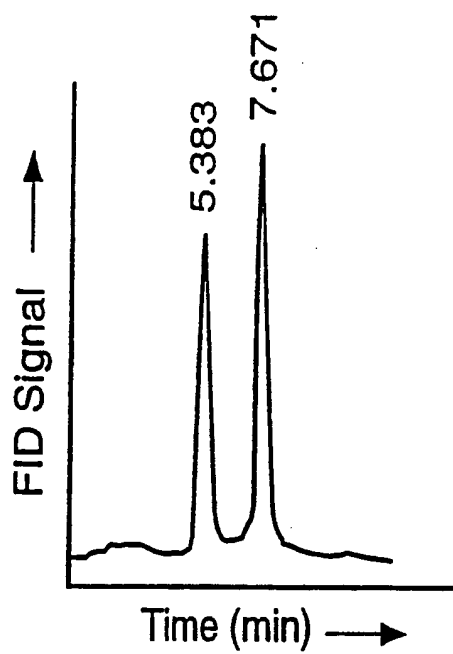
Before

FIG. 2 A

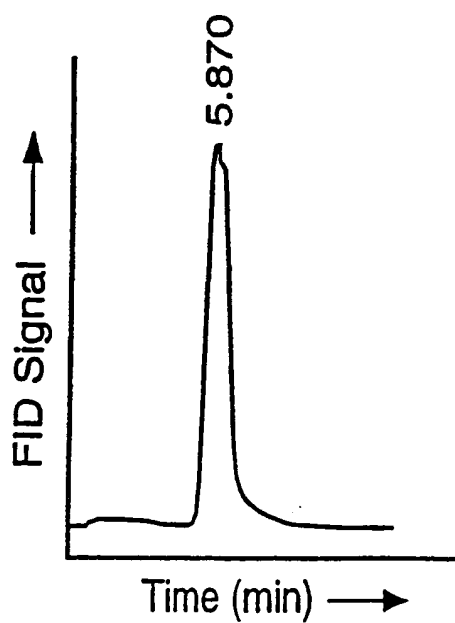
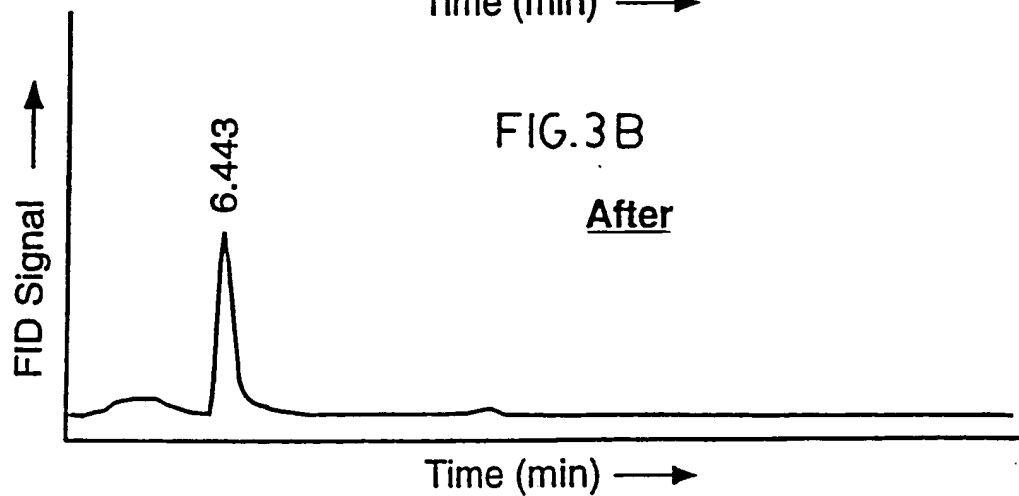
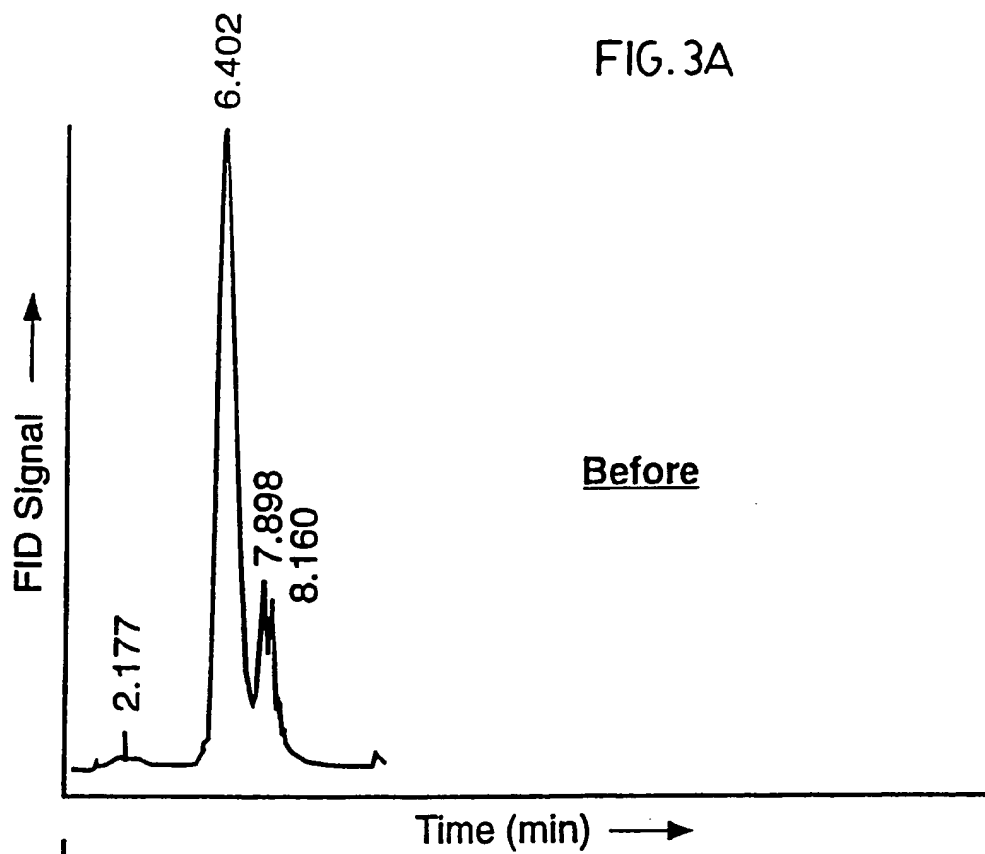
After

FIG. 2 B

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FIG. 3A

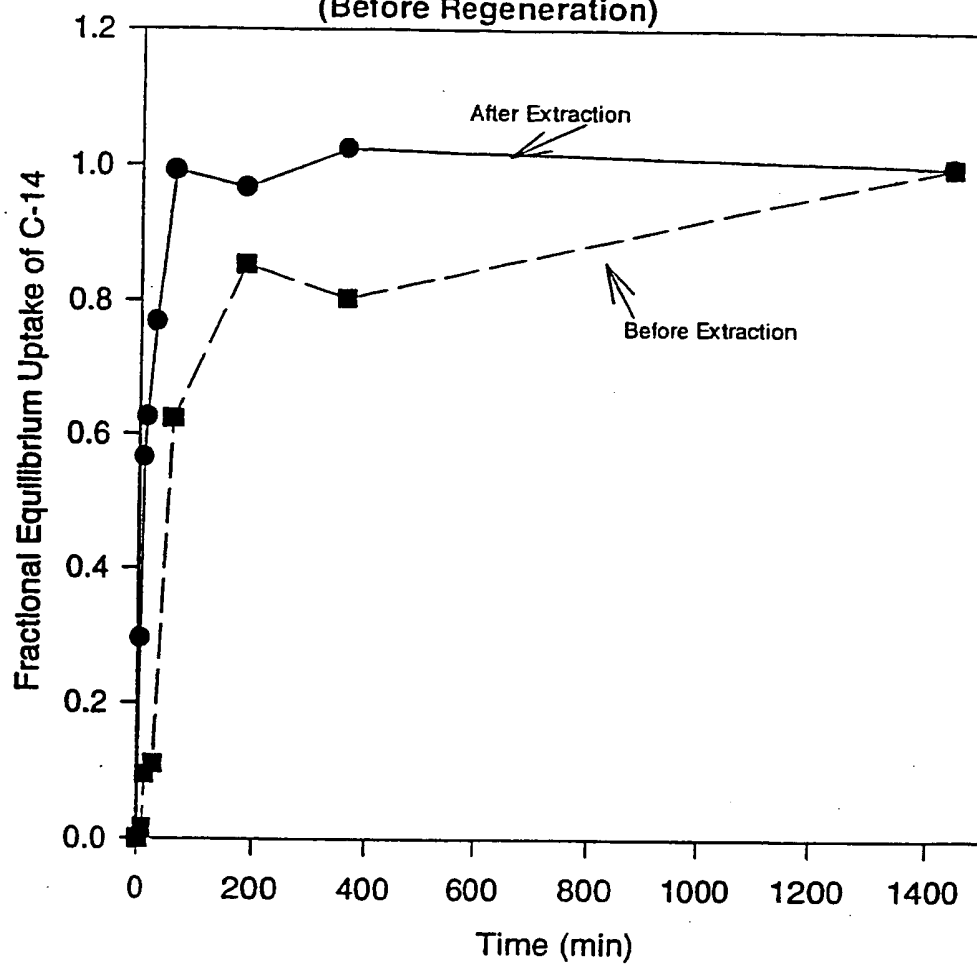


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Figure 4

Effect of SC-CO₂ Extraction on C-14 Uptake by Resins (Ambersep 440E/OH)
(Before Regeneration)

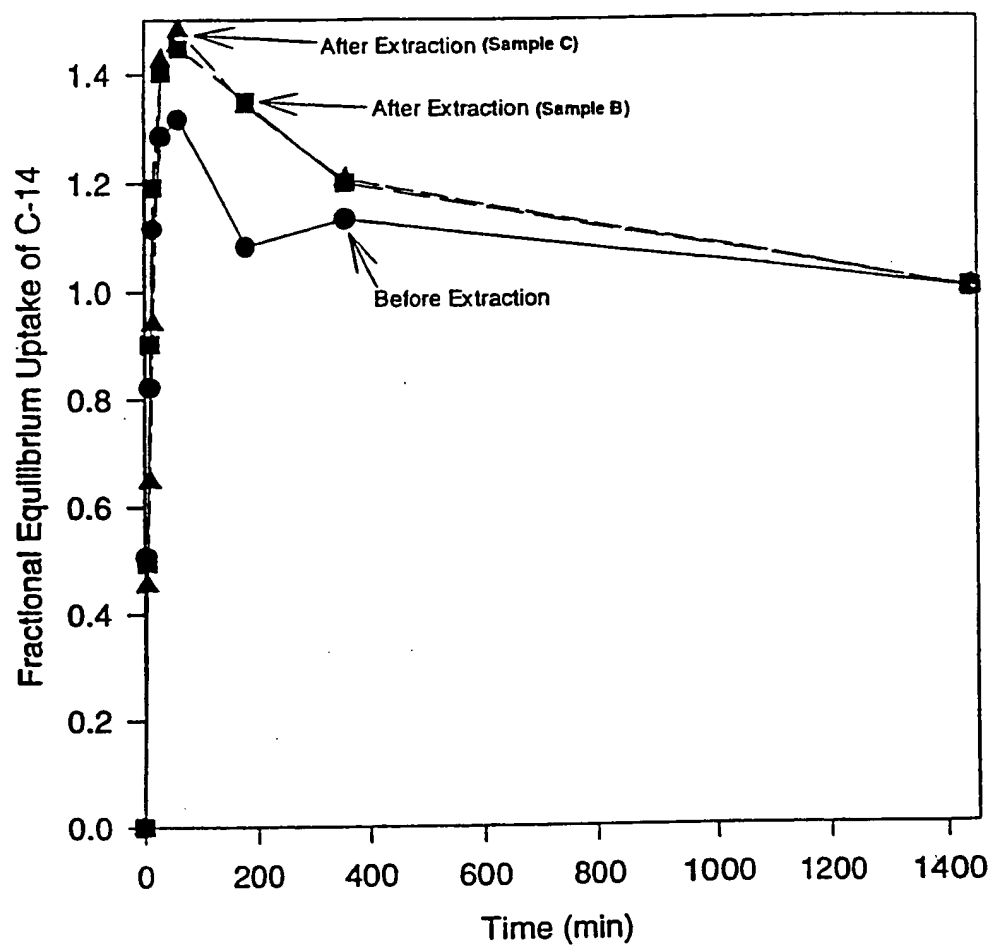


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Figure 5

Effect of SC-CO₂ Extraction on C-14 Uptake by Resins (Ambersep 440E/OH)
(After Regeneration to OH Form)

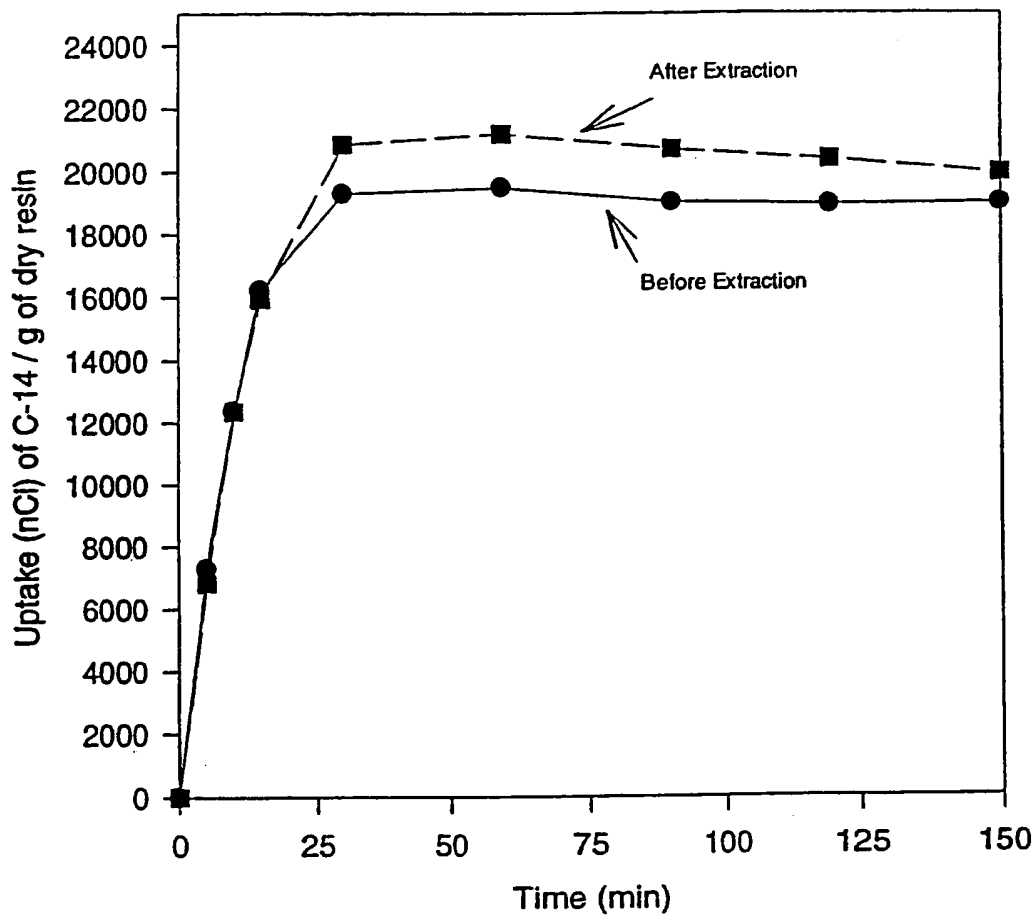


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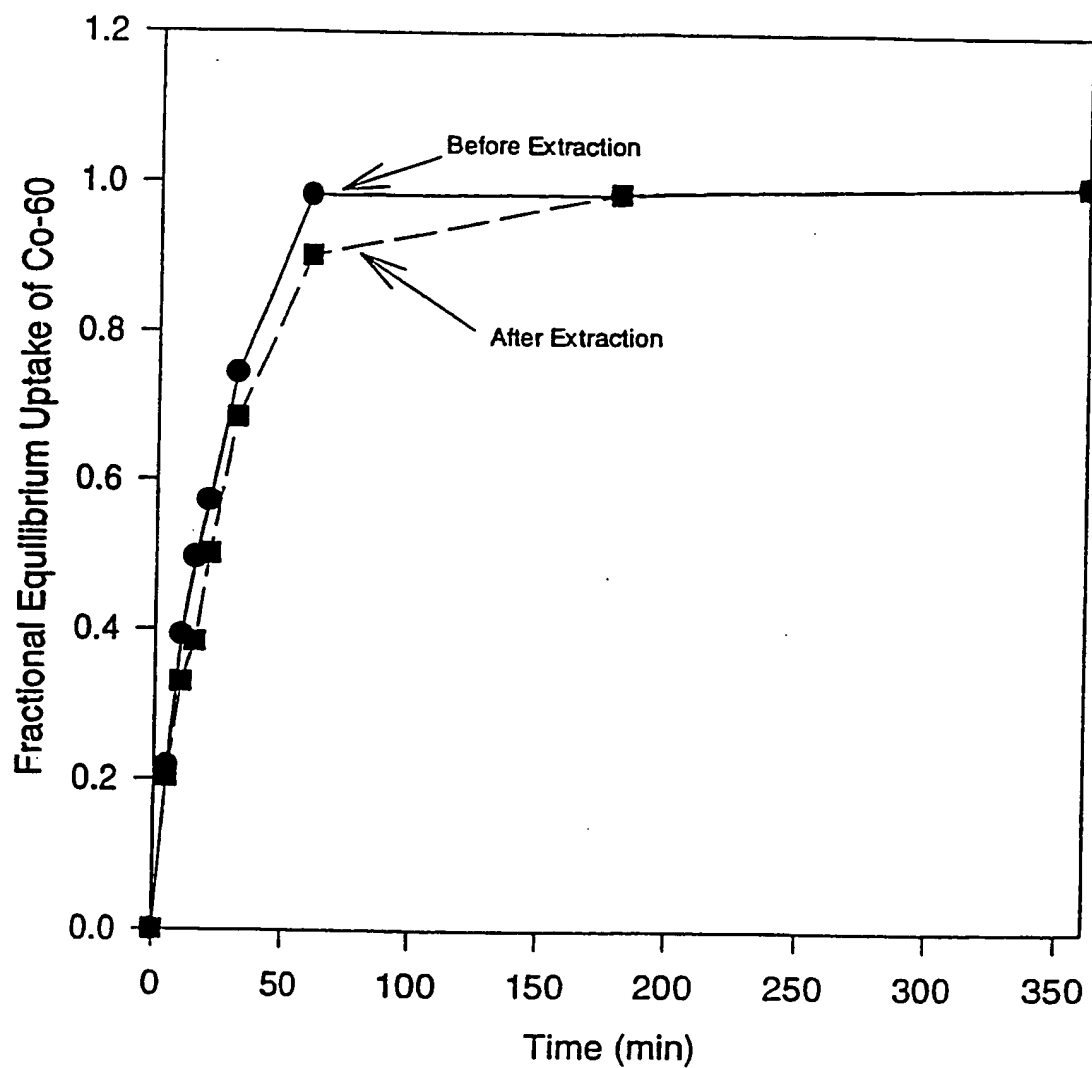
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Figure 6

Effect of SC-CO₂ Extraction on C-14 Capacity of Resins (Ambersep 440E/OH)
(After Regeneration to OH Form)



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Figure 7Effect of SC-CO₂ Extraction
on
Co-60 Uptake by Resins (Amberlite IR 120 Plus)

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/CA 00/00578

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J49/00 C08F6/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 698 153 A (MATSUZAKI HARUMI ET AL) 6 October 1987 (1987-10-06) the whole document column 2, line 23 - line 36 column 5, line 66 - column 6, line 5 column 6, line 30 - line 46; claims 1,3 ---	1,2,6,7, 9
A	DE 195 45 100 A (BASF AG) 5 June 1997 (1997-06-05) page 5, line 14 - line 25 ---	1,2,6,7, 9,15
A	US 4 061 566 A (M. MODELL) 6 December 1977 (1977-12-06) column 7, line 49 - column 8, line 3 --- -/--	1,2,6,7, 9,15

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

26 September 2000

Date of mailing of the international search report

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 198704 Derwent Publications Ltd., London, GB; Class A91, AN 1987-026161 XP002148403 & JP 61 283355 A (NIPPON RENSUI KK), 13 December 1986 (1986-12-13) abstract ---	1,2
A	WO 84 02291 A (HUGHES AIRCRAFT CO) 21 June 1984 (1984-06-21) page 2, line 3 - line 8; claims 1-5,8 page 5, line 3 - line 8 page 6, line 1 - line 22 ---	1,2,6-12
A	US 4 703 105 A (S.R. ALLADA) 27 October 1987 (1987-10-27) column 2, line 22 - line 24 column 6, line 4 - line 6 column 4, line 61 - line 68 ---	1,2,6,7, 9,11,12
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 01, 29 January 1999 (1999-01-29) & JP 10 265521 A (FUJI PHOTO FILM CO LTD), 6 October 1998 (1998-10-06) abstract -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 00/00578

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4698153 A	06-10-1987	JP 1593138 C JP 2015258 B JP 60166040 A DE 3504033 A	14-12-1990 11-04-1990 29-08-1985 08-08-1985
DE 19545100 A	05-06-1997	AT 183519 T DE 59602824 D WO 9720866 A EP 0865450 A ES 2135944 T JP 2000501443 T	15-09-1999 23-09-1999 12-06-1997 23-09-1998 01-11-1999 08-02-2000
US 4061566 A	06-12-1977	US 4124528 A CA 1064891 A DE 2544116 A DE 2716797 A GB 1522352 A JP 1247631 C JP 51061484 A JP 59024854 B	07-11-1978 23-10-1979 08-04-1976 27-10-1977 23-08-1978 16-01-1985 28-05-1976 12-06-1984
JP 61283355 A	13-12-1986	JP 1835384 C JP 4050859 B	11-04-1994 17-08-1992
WO 8402291 A	21-06-1984	EP 0127643 A ES 527786 A IT 1175802 B	12-12-1984 16-05-1985 15-07-1987
US 4703105 A	27-10-1987	NONE	
JP 10265521 A	06-10-1998	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)